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Confined Excitons, Phonons and their Interactions in Ge Nanocrystals Embedded in SiO₂

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Abstract We report the resonant Raman scattering of the optical phonon in Ge nanocrystals with radius ranging from 2 to 5 nm. We have observed the effect of quantum confinement on both the optical phonon and the E₁ exciton. The confinement energy of the E₁ exciton has been explained within the effective mass approximation.

1 Introduction

So far the effects of quantum confinement on excitons in semiconductor nanocrystals (to be abbreviated as nc) have been studied mostly near the fundamental band gap [1], although it is well known that there are several higher energy excitons in all the diamond and zincblende-type semiconductors. These higher energy excitons, such as the E₁ excitons, possess much larger oscillator strengths than that of the band gap excitons [2]. Furthermore, the E₁ excitons are hyperbolic excitons [2] and, therefore, behave quite differently from the parabolic band gap excitons. In order to observe confinement effects in these high energy excitons, it is necessary to use very large band gap material as barriers. In this paper we report a theoretical and experimental investigation into the effects of quantum confinement on the E₁ excitons and on the optical phonon in nc of Ge embedded in amorphous SiO₂. The experimental technique we have used is resonant Raman scattering (or RRS).

2 Experimental Details and Results

Three samples have been prepared by ion implantation of Ge ions into a thin layer of thermal oxide grown on a Si wafer following by annealing. Details of the sample preparation have been described elsewhere [3]. The nc size distribution was determined by high resolution TEM and x-ray diffraction [3]. The average diameters of Ge nc in these samples (labeled as Ge1 to Ge3) are 4, 7, and 10 nm respectively. RRS was performed by exciting the sample with tunable dye lasers with photon energies between 2 and 2.9 eV to cover the E₁ exciton energy (~2.2 eV) in bulk Ge. The Raman spectra of both the Ge nc and the Si substrate were recorded with a triple spectrometer equipped with a cooled CCD. The Ge optical phonon peak red-shifts and broadens asymmetrically as the nc size is decreased [4]. Both effects indicate that the Ge optical phonon is confined [5]. The integrated Raman intensity of the Ge confined phonon mode is normalized by the Si substrate Raman mode to minimize the effect of change in the optical alignment when the laser wavelength is changed. The resultant intensity after correction for the known dispersion of the Si Raman cross section is shown in Fig. 1 for all three samples. Notice that these spectra show significant enhancement in the Ge Raman intensity as a result of resonance with the E₁ exciton.

![Image](image_url)

**Fig. 1** The Raman cross section of the confined phonon mode in Ge nanocrystals normalized by that of the Si substrate plotted as a function of the excitation photon energy.

From the peak energies of these resonances we deduced the E₁ exciton energy in the nc and hence their confinement energy by comparison with the corresponding energy in bulk Ge. These confinement energies are tabulated in Table 1.

3 Model & Discussions

To explain the measured confinement energies we have used the effective mass approximation and assumed the confinement potential for both the electron and hole to be spherical and infinite. The effective masses of the electron and hole along the equivalent [111] directions (mₑ) are assumed to be infinite. The transverse reduced mass \( \mu_{tr}^{-1} = m_{tr1}^{-1} + m_{tr2}^{-1} \) of the E₁ exciton has been determined to be 0.045m₀, where m₀ is the free electron mass[6]. However, the individual

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Table 1 Experimental confinement energy of the E\textsubscript{1} exciton in Ge nanocrystals measured by resonant Raman scattering compared with theoretical values calculated within the effective mass approximation. The two theoretical values correspond to two different values for the ratio of the transverse effective masses m\textsubscript{tr}/m\textsubscript{h1}.

<table>
<thead>
<tr>
<th>Confinement Energy (eV)</th>
<th>Nanocrystal Radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Experiment</td>
<td>0.1</td>
</tr>
<tr>
<td>Theory (m\textsubscript{tr}/m\textsubscript{h1}=0)</td>
<td>0.12</td>
</tr>
<tr>
<td>Theory (m\textsubscript{tr}/m\textsubscript{h1}=1)</td>
<td>0.16</td>
</tr>
</tbody>
</table>

transverse masses m\textsubscript{tr} and m\textsubscript{h1} in the directions perpendicular to the [111] direction are not known. We have first assumed m\textsubscript{h1} to be infinite. With this simplification we have solved the Schrödinger equation for both the electrons and hole and obtained the ground state energies of the uncorrelated electron and hole pair (eh pair). The Coulomb attraction between the electron and hole is then calculated by perturbation theory using the ground state wave functions. Further details of the calculation can be found in [4]. The results are compared with experiment in Table 1. The theoretical result for the case where the transverse masses of the electron and hole are assumed to be equal [7] is also shown in Table 1 for comparison. We see that the agreement between theory and experiment is quite reasonable even considering the uncertainty in the transverse masses.

We note that the maximum Raman cross section of Ge1 in Fig. 1 is almost as large as that of Ge3 although Ge1 contains 3 times less Ge atoms. This suggests that the Raman cross section per Ge atom in Ge1 must be at least 3 times larger than that of Ge3. In this consideration we have not included a correction for the reduction in the Si substrate Raman intensity as a result of the Ge nc absorption. The importance of this correction is best seen by comparing the result in Ge2 with those of Ge1. If we neglect the attenuation of the incident radiation by the Ge nanocrystals then the measured Raman intensity in sample Ge2 should be about 2/3 of that in Ge3. However, the experimental values turn out to be 5 times weaker. This can be explained by a significant attenuation of the incident beam by the Ge nanocrystals before reaching the Si substrate. This suggests that the correction for Ge absorption should be significant also for the sample Ge1 so that the actual enhancement in the Ge scattering cross section in Ge1 relative to that in Ge3 is much larger than the factor of 3 as suggested by the relative amount of Ge atoms in these two samples.

4 Conclusions

In conclusion, we have observed via RRS confinement effects in both the optical phonon and the E\textsubscript{1} exciton in Ge nc's grown by ion implantation in SiO\textsubscript{2}. The measured exciton confinement energies are in agreement with model calculations based on the effective mass approximation.

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References